Flame-retardant Unsaturated Polyester Resin Incorporating Nanoclays

S. Nazaré*[1], B. K. Kandola and A. R. Horrocks

Centre for Materials Research and Innovation, University of Bolton, Deane Road, Bolton BL3 5AB

ABSTRACT

This work reports the use of polymer-layered silicate nanoclays as potential flame retardants in unsaturated polyester resins. Preparation, characterisation and flammability properties of polyester-clay hybrids have been studied. X-ray diffraction studies have provided evidence that dispersion of functionalised clays in the polymer matrix depends on the type of functional group of the organic modifier used. Flammability properties studied using cone calorimetry suggests that incorporation of nanoclays (5% w/w) reduces peak heat release rate (PHRR) by 23-27% and total heat release (THR) values by 4-11%. The fire growth rate index (FIGRA) is also reduced by 23-30 % following nanoclay inclusion. While incorporation of condensed-phase flame retardants such as ammonium polyphosphate, melamine phosphate and alumina trihydrate reduce the PHRR and THR values of polyester resin, the inclusion of small amounts of nanoclay (5% w/w) in combination with these char-promoting flame retardants causes total reductions of the PHRR of polyester resin in the range of 60-70 %. Ammonium polyphosphate, in particular

* Corresponding Author: Dr. Shonali Nazaré, Centre for Materials Research and Innovation, University of Bolton, Deane Road, Bolton BL3 5AB; Telephone: +44 1204 903118; Fax: +44 1204 399074.
e-mail address: sn4@bolton.ac.uk

and in combination with polyester-nanoclay hybrids show the best results compared to other flame retardants.

Keywords: Unsaturated polyester, Nanocomposites, X-ray diffraction, Flame retardants, Cone calorimetry, Montmorillonite, Clays

INTRODUCTION

Typical unsaturated polyester resins have both very poor resistances to fire and high smoke densities associated during burning because of their intrinsic chemical composition and molecular structures. Thus, to produce a polyester resin product with acceptable standards of flammability, very high quantities (> 30% w/w) of flame retardant additives are typically required[1]. Recent advances in nanoscience and nanotechnologies claim to offer benefits in achieving improved polymer properties[2] including that of flame retardancy. Studies have now confirmed that dispersion of functionalised clays in polymeric matrices to yield so-called nanocomposite structures enables them to exhibit reduced flammability alongside improved mechanical properties compared with conventional analogues[3]. This reduced flammability is generally observed as a reduced rate of heat release in a fire as well as enhanced char formation. It is considered that formation of this carbonaceous-silicate char builds up on the polymer surface during burning, which insulates the underlying material and slows the mass loss rate of decomposition products[4]. However, while the presence of nanoclays alone cannot confer acceptable levels of flame retardancy, recent research on flammability of thermoplastic polymer-clay nanocomposites in the presence of conventional

flame retardants has reported[4-7] that when both a nanoclay and a char-forming flame retardant are present, the threshold concentration, I_c[8] of flame retardant required can be significantly reduced.

In the recent literature, 50-70% reductions in peak heat release rate have been reported for various polymer (e.g. nylon 6, polystyrene, polypropylene)-clay nanocomposites[2].The magnitude of the flammability reduction depends upon the type of the polymer, the character of organic modification of the functionalised layered-silicate and the amount of clay present in the polymer[5]. Furthermore, the reduction in PHRR of nanocomposites is in general dependent on the incident heat flux and in some cases the fire retardancy provided by nanocomposites recedes with decreasing incident heat flux[9]. In addition to the incident heat flux, cone calorimetric measurements are sensitive to sample thickness. For thermally thin materials the temperature is almost constant throughout the depth and hence the gasification rate more rapid than in thermally thick sample with a temperature gradient and lower gasification rate[10]. Kashiwagi et al have shown that the effectiveness of flame retardancy of nanocomposites, as measured by cone calorimetry, becomes less with thinner sample compared to thicker samples[11]. This is due to the fact that the thicker sample has more clay to cover same exposed area as compared to thinner sample of same surface area.

Of particular interest to our research, is that while the preparation, characterisation and improved mechanical/physical properties of unsaturated polyester-clay nanocomposites have been reported[12-16], no comments upon possible improved fire performance have been included. We have also prepared similar structures by in-situ polymerization using commercially available functionalised nanoclays as well as organically modified nanoclays with and without conventional flame

retardants[17,18]. Thermogravimetric studies of polyester-clay nanocomposites reported earlier[17] have shown that addition of nanoclays lowers the decomposition temperature and thermal stability of a typical resin upto 600 ^{o}C. Above 600 ^{o}C the trend is reversed in a region where carbonaceous residual chars only remain[17]. Inclusion of condensed phase-acting flame retardants enhances char formation of the resin above 400 ^{o}C and additional presence of nanoclays promotes further increase. However, enhancement in char formation is not as great as expected when compared with other similar polymer-clay nanocomposite structures[4]. Thermal analytical techniques however are not representative of real fire situations, hence our earlier studies have been extended to determine the fire performance of polyester-clay hybrids with and without flame retardants by using cone calorimetry and are reported here.

EXPERIMENTAL

Materials

Resin: Polyester resin - Orthophthalic, Crystic 471 PALV (Scott Bader).

Clays: Details of commercially available functionalised nanoclays (Southern Clay Products, USA) used in this study are given in Table 1.

Flame-retardants (FR): The following commercially available flame retardants were used without further purification:

(i) APP - Ammonoium polyphosphate (Antiblaze MCM, Rhodia Specialities),

(ii) NH - Melamine phosphate (Antiblaze NH, Rhodia Specialities),

(iii) NW - Dipentaerythritol / melamine phosphate intumescent mixture (Antiblaze NW, Rhodia Specialities)

(iv) ATH - Alumina trihydrate (Martinal, Martinswerk, GmbH).

Equipment

X-ray diffraction (XRD) studies were carried out using a Siemens D500 powder diffractometer with a step size of 0.02^{o}, a step time of 1s and a range of $0\text{-}25^{o}$ on the 2-theta scale. Simultaneous DTA-TGA analysis was performed using an SDT 2960 TA instrument under flowing air (100 ml/min) and at a heating rate of 10K min^{-1} on 25 mg sample masses. A cone calorimeter (Fire Testing Technology Ltd., UK) was used at an incident heat flux of $50kW/m^2$ according to ISO 5660.

Preparation of polyester-nanoclay hybrids

The polyester-clay nanocomposites have been prepared by in-situ intercalative polymerization. The required amount of a given clay (5 – 10 %, w/w) was gradually added to the polyester resin, while stirring with a mechanical mixer under high shear (900 rpm) for 60 min at room temperature. For samples incorporating flame retardant (FR), a defined amount (20 – 30 % w/w) with respect to resin-clay mixture) was added to the mixture of resin and clay after 20 min of mixing. Actual percentages of various components in the formulations are given in Table 2. Samples were cast and cured at room temperature followed by post-curing at 80 ^{o}C for at least 8 hours. According to ASTME E 1354/ISO 5660 standard for cone calorimetric testing, the samples are classed as thermally thin samples (3 mm ± 12%).

In order to determine an appropriate level of nanoclay loading and the amount of flame retardant microparticles that can be added to the resin so as to render the formulation processable and to achieve optimal flame retardant properties, a range of samples given in Table 3 was prepared with different percentages of nanoclay and flame retardants. For this set of samples, the unsaturated

polyester resin was diluted with methyl methacrylate (MMA) (5% w/w). With diluted resin, clay levels could be added upto 10% (w/w) with respect to polyester resin. Samples containing 5, 7.5, 10% (w/w) clay (Cl 25A), each with and without 20 and 30% (w/w) APP were prepared and formulations are listed in Table 3. For higher clay concentrations (> 5% clay) in the presence of FR, the cross-linking reaction was noticeably slower and hence not processable. It was evident that the formulation became more plastic and difficult to cure, which may be the consequence of dispersed nanoclays interacting with the polymerising structure, by possibly obscuring cross-linking sites and hence reducing rates of curing of samples. This has also been observed by Bharadwaj et al[16], and they have proposed that the crosslink density is inversely proportional to the degree of exfoliation and macroscopic dispersion. The cross-linking density apart from affecting curing of the thermosetting resin, also influences its thermal decomposition. Less cross-linking will reduce charring tendency of the resin, resulting in reduced flammability of the sample. However, in this work, the effect of additives on curing was not measured quantitatively, but will be discussed qualitatively based on parallel thermal analytical behaviour of these same samples in a separate publication. The following analyses and discussions assume that while the effect of curing level variation (if any) is not known and since all samples were sufficiently cured to have acceptable mechanical coherence to enable further study, levels of curing were not in fact greatly dissimilar. The samples which had difficulty in curing (suggesting different rates of curing) have not been excluded from further study. Based on the initial cone calorimetric results of this study shown in Table 3 coupled with observations on formulation and processability, samples containing 5% clay with 20% FR loadings were selected for more comprehensive study by XRD and cone calorimetry. Samples with different combinations of nanoclays and flame retardants as given in Tables 4-6 were prepared. For this set of samples additional MMA was not used.

RESULTS AND DISCUSSION

While the detailed analysis and discussion of thermal analytical results for such samples are reported elsewhere[17], here sample thermal stability is assessed in terms of percentage char residue at 600 and 800 ^{o}C. In summary, and to provide information relevant to the cone calorimetric results, the thermogravimetric data in Table 3 show increased mass residues with increased clay loadings. After taking % silica content in the residue (values taken from reference 17) into account, the percentage mass residue at 800 ^{o}C for 10 % (w/w) clay loading has increased from 2.7 to 5.1%. In the presence of APP alone, char values at 600 ^{o}C show increases at 20 and 30% loadings, although values at 800 ^{o}C are far lower. For Res/Cl/APP samples containing 20% APP, increasing clay levels has increased char residues at both 600 and 800 ^{o}C. However, samples with 30% APP show only slight decreases at 600^{o}C and only further increases in char yield at 800^{o}C as clay content increases from 5 to 10% with respect to the Res/APP analogue sample values. This may be because high clay and FR contents in the resin reduce the cross-linking efficiency of the resin, resulting in less char formation .

X-ray diffraction studies

Interlayer spacing of the clay platelets for nanoclays alone as obtained by X-ray diffraction studies are given in Table 1. The basal spacing for sodium montmorillonite clay has increased in organically modified clays from 1.17 nm to 1.76 - 3.15 nm, depending on the type of organic modification. Decreases in 2θ angle and hence increases in basal spacings are due to replacement of small Na^{+} ions present by large organic cations in the organically modified clays. The chemical

structure of the organic modifier in the clay will also influence the dispersion of clay in the polymer matrix and its tendency to intercalate and exfoliate.

In addition to transmission electron microscopy (TEM), which was not available for this study, the characterisation of nanocomposite structures in a polymer can be identified by monitoring the position, shape and intensity of the basal spacing in the lower 2θ region (2-10^o). XRD patterns for resin-nanoclays hybrids are given in Figure 1(a) and the characteristic peaks, the 2θ angle and corresponding d-spacing values in the lower 2θ region (2-10^o) are given in Table 4. Diffraction peaks of clays 10A, 15A and 30B at 4.5^o, 2.8^o and 5.1^o (see Table 1) are seen in XRD patterns of Res/Cl 10A, Res/Cl 15A and Res/Cl 30B samples at 5.0^o, 2.4^o and 4.7^o respectively (see Figure 1(a) and Table 4). For the Res/Cl 10A sample, the diffraction peak has moved slightly to a higher angle (from 4.5 to 5.0^o) suggesting a degree of contraction of the clay layers. In fact, there is little XRD evidence that the introduction of this clay has generated a nanocomposite structure, which may be attributed to the poor chemical affinities between the organic modifier present on Cl 10A and the polyester monomer and polymer; hence, reducing the affinity of the functionalised clay with resin monomers and respective repeat units. However, in the X-ray diffraction pattern of the Res/Cl 15A hybrid in Figure 1 (a), two prominent sharp peaks are seen. The characteristic peak of Cl 15A at 2.8 ^{o} has moved slightly to the lower angle (2.4^o) indicating a small increase in d-spacing from 3.15 to 3.57nm. This suggests that ordered intercalation of the polymer chains into the organoclay layers has occurred, however, the nanoclay dispersed in polyester matrix did not lose its ordered platelet structure via complete separation or exfoliation. Thus, the Res/Cl 15A hybrid probably has an intercalated nanocomposite structure. The second characteristic peak seen at 4.8^o,

which is double the value of the first characteristic peak (2.4^{o}), is due to secondary diffraction of the silicate layers (d_{002})[18].

The characteristic peak for the clay Cl 25A corresponding to basal spacing of 2.02 nm at $2\theta = 4.4^{o}$ is absent in the XRD pattern for Res/Cl 25A (see Figures 1(a) and (b) and Table 1) suggesting the disordering and loss of structural regularity of the clay layers and hence possible formation of an exfoliated nanocomposite structure. However, in contrast, for Res/Cl 30B, the characteristic peak of the clay has moved from $2\theta = 5.1^{o}$ (see Table 1) to 4.7^{o} (see Table 4 and Figure 1(a)), resulting in increased d-spacing from 1.76nm to 1.856 nm. Thus, the Res/Cl 30B sample represents a possible intercalated structure where polymer chains have separated the clay lamellae while still maintaining the overall ordered structure of clay. Based on X-ray diffraction studies, Bharadwaj et al[16] have shown formation of exfoliated nanocomposite structure using Cloisite 30B clay. However, TEM studies on the same sample at different length scales showed a random dispersion of intercalated/exfoliated aggregates throughout the matrix. Thus, XRD data is not sufficient to characterise nanocomposite structure conclusively. Nevertheless, in this work, XRD data has been used to compare nanocomposite structures depending on using different commercially available functionalised clays. It is evident from these results that the degree of dispersion of the nanoclay is related to its functional group character. Cl 15A is non-polar, whereas 30B has polar –OH groups. Both however, have linear aliphatic chains resulting in intercalation. The benzyl group present in the Cl 10A apparently neither promotes intercalation nor exfoliation, which might be due to steric hindrance preventing close contact with resin. The functionalised clay Cl 25A has a cyclohexyl group present, which in chair form can be quite planar and interact with resin phenyl (phthalyl) groups, resulting in possible exfoliation.

The presence of flame retardant appears to have little effect on the surrounding resin/clay nano/microcomposite formation. X-ray diffraction patterns of pure APP, Res/APP and Res/Cl 25A/APP are shown in Figure 1(b) and peak values are given in Table 4. Crystalline peaks of APP at $2\theta = 14.6^{o}$ and 16.2^{o} are also seen in XRD curves for Res/APP and Res/Cl 25A/APP samples. Characteristic peaks due to presence of clay in Res/Cl/APP samples except those containing Cl 25A are noted at similar 2θ angles as in respective Res/Cl samples given in Table 4. Hence, X-ray diffraction studies indicate that inclusion of flame retardants neither influences nor facilitate nanocomposite formation.

Cone calorimetry

Under cone calorimetric conditions at 50 kW/m^2 heat flux, unsaturated polyester ignites at 34 s and burns for 136s yielding a PHRR of 1153 kW/m^2 and total smoke released is 761 litres (see Table 3 and Figures 2 (a) and 3). Effective heat of combustion (H_c), which reflects the calorific value per unit of the specimen for unmodified polyester resin, is 21.1 MJ/kg and fire growth rate index (FIGRA), which is defined as the ratio of PHRR and the time at which PHRR occurs, is 11.5 kW/s (see Table 5). The rate of smoke released sharply increases to about 60 l/s (see Figure 4(c)) and as the combustion of polyester resin occurs vigorously, the specimen is quickly burnt out and the rate of smoke release rapidly decays.

Cone calorimetric data in Table 3 shows no change in peak heat release rate for resin diluted with MMA although its presence reduces THR although within error, the values may be identical. An increase in clay loading from 0% to 10% (w/w) decreases PHRR from 1154 to 705 kW/m^2 and

increases TTI slightly from 32s to 37s as seen from Figure 2. Figure 3 shows the PHRR value as a function of clay loading and it can be seen that there is a linear relationship between PHRR and clay content ($R^2 = 0.93$). Higher clay loading results in formation of a thicker insulating layer on the surface of burning polymer, thus providing potential barrier to both mass and energy transport[19]. There is a corresponding decrease in THR values and effective heat of combustion which is probably due to reduced fuel content in sample containing higher clay levels. The amount of smoke released increases slightly with increased clay loadings. Increasing FR concentration from 20% to 30% shows a slight decrease in PHRR and smoke values. Of the processable Res/Cl/FR samples, that containing 20% APP shows a significant decrease in PHRR value to 417 kW/m^2 and this is less than resin samples containing only 20% or 30% APP. Thus relative to these clay-free samples, the combined clay-APP formulation shows better fire performance even if crosslinking is less in the Res/Cl/FR sample compared to Res/Cl and Res/FR samples.

Cone calorimetric data for the various samples containing 5% clay and 20 (w/w) FR are reported in Tables 5 and 6. Selected results are also graphically shown in Figures 4 - 7. The test results presented here are averages of three replicates for each sample and reproducibility of results is within ± 6 % co-efficient of variation.

Effect of nanoclays on flammability of polyester resin

In Figure 2 HRR versus time curves for resin and Res/Cl 25A nanocomposite structures having different percentages of clay levels are shown. With increasing clay levels, the HRR versus time curves have reducing maxima and become broader (see Figure 2(a)), indicating that samples burn less intensely (shown by reductions in PHRR) but for longer times. There is also corresponding slight decrease in the effective heat of combustion with increased clay levels. Higher flame-out

times for samples containing clay result in increasing total smoke release values as can be seen in Table 3. The clay-rich hybrids (mass fraction of ~ 10% w/w) reflect properties dominated by the inorganic phase as can be seen by the mass loss curves in Figure 2(b) where samples with higher clay content show better thermal stability as the burning progresses. Enhanced thermal stabilities for samples with higher clay concentration are in agreement with thermogravimetric results in Table 3.

All nanoclays show similar cone calorimetry trends as for Cl 25A discussed above. The cone calorimetric data for different formulations with different clays present at 5% (w/w) levels are given in Table 5 and selected cone parameters for Res/Cl 10A sample are graphically shown in Figure 4. Surprisingly, the introduction of each clay has not reduced respective sample effective heat, Hc values below that of the resin (21.1 Mj/kg) in spite of their having replaced otherwise combustible resin. However, while all Hc values listed in Table 5 for resin-clay combinations are similar, any real reductions might be masked by experimental error.

Selected cone parameters from Table 5 for all the Res/Cl samples are plotted as percentage reduction of values with respect to pure resin in Figure 5 (a). The percentage reductions in PHRR values of polyester-clay hybrids (23-27%) are lower when compared with other polymer-nanocomposites where the reductions in PHRR in the range of 50-75% have been reported[21]. This could probably be due to the rupturing of protective surface layer of the clay particles formed during radiant heat exposure as a consequence of violent gasification during cone calorimetric experiments; highly audible cracking noises were noted, indicative of explosive gasification. Ideally, for optimal reduced fire performance of nanocomposites, the clay particles should cover

the entire surface of the sample and remain coherent over the entire burning period[22.] Visual observations during cone calorimetric experiments confirmed that vigorous bubbling and bursting did occur as soon as the samples were exposed to the heat flux.

With respect to the PHRR values of all Res/Cl samples, Table 5 shows the apparent decreasing order Cl 10A > Cl 30B > Cl 15A > Cl 25A (relating to the order microdispersed > intercalated > exfoliated as indicated by XRD studies) although the whole spread of values falls in a range of ±6% which is commensurate with the error expected of cone calorimetric data. With regard to correlating improved fire performance with nanocomposite structure, particular attention is drawn to the behaviour of the Cl 10A clay. The X-ray diffraction results in Table 4 and Figure 1 (a) and cone calorimetric data in Table 5 and Figure. 5(a) indicate that although nanocomposite structure is not observed following XRD study of the Res/Cl 10A hybrid, the apparent microcomposite exhibits the highest reduction (27%) in PHRR as compared to other intercalated (Res/Cl 15A and Res/Cl 30B) and exfoliated (Res/Cl 25A) nanocomposites. However, while bearing in mind the comments above about experimental error, the Res/Cl 25A sample, which shows complete exfoliation of silicate layers, has the highest apparent PHRR value (887 kW/m^2, see Table 5) of all resin-clay hybrids reported. This suggests that despite the exfoliated nanocomposite structure, the subsequently formed protective barrier might have collapsed as the temperature increased, thus opening channels to permit the escape of volatile products from burning polymer into the flaming zone thereby increasing PHRR. Lower apparent reductions in peak heat release rate in exfoliated Res/Cl 25A hybrid might also be attributed to the cross-linking density of the sample which could sequentially affect thermal degradation[16] and hence heat release properties of the polymer. As stated previously, however, we have not determined cross-linking levels within or differences

between resin composite samples in this study. Furthermore, the THR value of the Res/Cl 25A sample is the lowest reported for clay-containing samples in Table 5 and although at the extreme of the experimental 6% error level and could be considered to be real; also the total burning time is significantly reduced in this sample (FO = 147s) compared to the other samples. Thus the better fire performance properties of the Res/Cl 10A sample, despite apparent microcomposite morphology, is not clearly understood. Qin et al[23] have proposed that the thermal degradation of organoclays leads to formation of acidic sites on clay layers which can catalyze the dehydrogenation and cross-linking of polymer chains. They have also shown that there exists a physical cross-linking network structure composed of clay particles and polymer chains in polymer-clay hybrids. These physical and chemical cross-linking effects, depending on the organic modifier on the clay, can result in increased thermal stability and reduction in PHRR. In addition, while volatile degradation products could also have been chemically adsorbed on silicate layers, this latter might be expected to be similar for all clays used in this study. Finally and in conclusion, while FIGRA values are reduced by 22-30% for Res/Cl samples, the amount of smoke generally is shown to increase with inclusion of each nanoclay.

Effect of conventional flame retardants on flammability of polyester resin

Of the chosen conventional flame retardants selected, ammonium polyphosphate, in general, is effective in the condensed phase and moreover, ammonium salts of phosphoric acids are known to be effective in thermoset resins[1,24]. On the other hand, melamine phosphate acts additionally as a foaming agent, catalyst and a char former by promoting intumescence which may be enhanced by dipentaerythritol. In contrast, alumina trihydrate acts mainly as a filler and dilutes the polymer,

thus reducing the concentration of decomposition gases. It also endothermically releases water vapour to cool the pyrolysis zone at the combustion surface[8].

Cone calorimetric parameters for all the Res/FR samples given in Table 5 are plotted as percentage reduction of values with respect to pure resin in Figure 5 (b). Amongst the conventional flame retardants used in this study, melamine phosphate (NH) shows highest reduction (53%) in PHRR of polyester resin followed by ammonium polyphosphate (52%) and alumina trihydrate (ATH) (45%). Melamine phosphate with dipentaerythritol in Antiblaze NW does not seem to be very effective in lowering the peak heat release rate of unsaturated polyester (25%), however. Increasing APP concentrations from 20% to 30% (see Table 3) does not show any significant change in cone calorimetric parameters considered here except that the amount of smoke released is reduced with an increase in APP concentration. Surprisingly, flame retardants present at 20% (w/w) slightly lower the TTI of the resin except for alumina trihydrate, which due to its endothermic decomposition, liberates water vapour and thus dilutes the pyrolysis gases and so increases the ignition time of polyester resin. Flameout times for all the Res/FR samples are considerably increased (159-205s), as expected compared to the pure resin sample (136s). Although the burning times measured in terms of flameout time are increased with the addition of flame retardants, the THR results in Figure 5 (b) show reductions for all Res/FR formulations compared to the control sample. Mass loss curves in Figure 4 (d) show enhanced char formation with APP and this is shown to be the case for all retardants as seen by increased mass residues in Table 5. Amount of smoke released plotted as a function of time for the Res/APP sample in Figure 4 (c) indicates a lower rate of release compared with the pure resin sample. With regard to the other flame retardants, it can be seen from Table 5 that ATH and NH are moderately effective in

lowering the level of smoke generation while the addition of dipentaerythritol in Antiblaze NW, indicates a significant increase in smoke level. Finally, effective heat of combustion and FIGRA values for all Res/FR samples are significantly lowered, thus showing that all flame retardants are effective on polyester resin.

Combined effect of nanoclays and flame retardants on polyester resin

From Table 5 and as discussed earlier, it can be noted that the nanoclays alone reduce flammability of polyester resin only marginally while flame retardants, and in particular APP and NH, are effective in reducing flammability considerably (see Figure. 5 (b)). Although all combinations of Res/Cl/FRs at 5% clay and 20% FR levels were studied, only selected and representative results are reported in Table 6 and derived cone data are graphically plotted for the Res/Cl 10A/APP sample in Figure 4. The effects of adding each different modified clay to the Res/APP (20%) formulation are shown in Figure 6 and the effects of each different flame retardant added to Res/Cl 25A (5%) mixtures is reported in Figure 7.

From Figure 4 (a) it can be seen that the PHRR for the Res/Cl10A/APP sample is significantly reduced from 1153 kW/m^2 for unmodified resin to 357 kW/m^2, which represents a decrease below the figure of 456 kW/m^2 for the flame retardant alone (i.e., Res/APP in Table 5). Because of the associated longer time taken to reach peak heat release, a significantly reduced FIGRA index of 2.9 kW/s results. Reduced THR and peak smoke values in Figures 4 (b) and (c) respectively also suggest enhanced fire performance. Mass loss rates in Figure 4 (d) show enhanced thermal stability of Res/Cl10A/APP sample compared to those with and without APP or with clay alone. In all resin-clay-APP formulations, it is proposed that the clay reacts with released polyphosphoric acid

to form a thermally stable ceramic coating. Bourbigot *et al*[25] have suggested that the nanoclay allows the thermal stabilization of a phosphorocarbonaceous structure in the intumescent char, which increases the efficiency of the shield, and, forms a ceramic layer which can act as a protective barrier, limit oxygen diffusion and reduce heat transfer through the char layer. Similar phenomena have also been noted by Beyer[26] for polyester nanocomposite formulations containing ATH. However, the percentage reductions in flammability as a consequence of combining clay and flame retardant in Res/Cl/FR formulations are relatively minor when compared with Res/FR samples (see Figure 6(b) and Figure 7(b)), whereas significant reductions in flammability parameters, particularly PHRR (60-70%) and FIGRA (50-75%) values are seen when compared with pure resin (see Figure 6(a) and Figure 7(a)).

With regard to use of FR in combination with different nanoclays, results in Figure 6 indicate that the improvement in fire performance of Res/Cl/FR formulations with respect to Res/FR samples appears to depend on the nature of organic modification of the clay. Res/Cl 10A/APP shows greatest improvement in fire performance (as PHRR and FIGRA) compared with the Res/APP and the other Res/Cl/APP formulations; however, THR values are not reduced further and in fact show slight increases with respect to Res/FR analogue sample values (see Figure 6 (b)) in spite of their introduction being at the expense of an equal mass of resin and hence fuel. (see Table 2). This same effect is observed when adding each FR and Cloisite 25A to resin as shown in Fig. 7(b). Clearly, given the associated accompanying reductions in PHRR and FIGRA values (except for the Res/Cl25A/NH combination), this general increase in THR as consequence of clay addition is difficult to explain, although its magnitude appears to be both clay and FR dependent. If the effect is real, then the reduced fuel element from the reduced resin content must be more than

compensated by a modification to the resin pyrolysis mechanism that enables more fuel to be generated. More work to investigate this effect further is essential in order to confirm it and, if true, to study its cause.

Generally, (see Table 6 and Figure 7) when any clay, exemplified by Cl 25A, is added to the resin containing a conventional flame retardant, a slight increase in TTI and small reductions in PHRR and FIGRA values are observed compared to respective Res/FR samples. Only in the Res/Cl 25A/NH formulation does the clay appear to have a detrimental effect on cone calorimetric parameters with respect to Res/NH samples (see Figure 7 (b)). On the other hand, Cl 25A addition is most effective with melamine phosphate/dipentaerythritol (NW) and alumina trihydrate (ATH). Formulations with ATH, however, show consistent decreases in flammability properties due to its endothermic decomposition as explained before. Smoke generation, while being very slightly increase with addition of clay for APP, NW and ATH is nearly doubled for the NH-containing formulation. Presumably the absence of dipentaerythritol from the latter has a significant effect in this respect.

CONCLUSIONS

X-ray diffraction studies have suggested that intercalation of polyester chains and formation of a possible nanocomposite structure depends on type of organic modification of nanoclay. Exfoliated nanocomposite structures may be obtained by appropriate selection of functionalised nanoclay. It is proposed that cyclohexyl groups in Cl 25A interact with phenyl groups of the unsaturated polyester resin, resulting in exfoliated nanocomposite structures whereas linear aliphatic chains in Cl 15A and Cl 30B give possible intercalated nanocomposite structures. It is also suggested that the benzyl

group in Cl 10A causes steric hinderance with polyester resin to give only a microcomposite structure. Cone calorimetric studies coupled with X-ray diffraction suggest that the improved flammability properties of polyester-clay hybrids are not always dependent on formation of nanocomposite structures. Increased flame retardancy might be partly due to the physical and thermal cross-linking of clay particles and polymer chains and/or physico-chemical adsorption of the volatile degradation products on the silicates, which is also dependent on the organic modification of montmorillonite. However, notwithstanding the lack of a clear nano-structural dependence, a significant conclusion is that when a clay is present with a conventional flame retardant PHRR values of polyester resin could be reduced by as much as 40-70% in total although the contribution by the clay present is significantly less and in some cases almost negligible and in the case of Antiblaze NH presence, negative. Thus, apart from this latter case, fire performance, in terms of reduction in the propensity to spread flame, is still generally improved compared with the flame retardant when present alone. The mechanical performance in terms of flexural moduli and stress-at-failure for the samples containing nanoclays with and without flame retardants has been studied and presented elsewhere[18]. This indicates that inclusion of functionalised nanoclays enhances mechanical performance of resin, which incidentally, provides further evidence for nanocomposite structures being present in spite of the absence of TEM data. More detailed discussions on the effect of nanoclays on both mechanical and fire performance of glass-reinforced composites will be given in a subsequent publication.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the financial support from the Engineering and Physical Science Research Council (EPSRC Grant GR/60690/01) during this work and National Institute of

Standards and Technology (NIST), USA for their technical and financial support. The authors also want to thank Scott-Bader for providing resin sample and technical support.

References

1. Hörold S. Phosphorus flame retardants in thermoset resins. *Polym Deg Stab.* 1999; **64**: 427-431
2. Kandola BK , *Nanocomposites, Fire Retardant Materials*, Horrocks AR and Price D (eds). Woodhead Publishing Ltd: Cambridge, 2001; chapter 6, 204-219
3. Ray S S and Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog. Poly. Sci*. 2003; **28**:1539-1641
4. Gilman JW, Kashiwagi T, Morgan AB, Hariss RH Jr, Brassell L, Awad WH, Davis RD, Chyall L, sutto T, Trulove PC, DeLong H. In *Proc. Conference Fire and Materials*, Interscience Communications: London, 2001; 273-284
5. Wilkie C. Recent advanced in fire retardancy of polymer-clay nanocomposite. In *Recent Advances in Flame Retardancy of Polymers*, vol 13, Lewin M (ed). Business Communications Co Inc.: Norwalk, 2002; 155-160
6. Horrocks AR, Kandola B, Padbury SA, Nanocomposite fibre-forming polymers as potential fire protective materials. In *proceedings of Flame Retardants 2004 Conference*, Interscience Communications Ltd, Flame Retardants 2004; 97-108 ISBN 0 9541216 2 7.
7. Bras M. Le, Bourbigot S, Delporte C, Siat C, Tallee Y Le, New intumescent formulations of fire-retardant polypropylene-Discussion of the free radical

mechanism of the formation of carbonaceous protective material during the thermo-oxidative treatment of the additives. *Fire Mater*.1996; **20**: 191-203

8. Zhang S, Horrocks AR. A review of flame retardant polypropylene fibres. *Prog. Polym. Sci*. 2003; **2**: 1517-1538
9. Bartholmai M, Schartel B. Layered silicate polymer nanocomposites: new approach or illusion for fire retardancy ? Investigation of the potentials and the tasks using a model system. *Polym. Avd. Technol.* 2004; **15:** 355-364
10. Nazare S, Kandola B, Horrocks AR. Use of cone calorimetry to quantify the burning hazard of apparel fabrics. *Fire Mater*. 2002; **26**: 191-199
11. Kashiwagi T, Shields JR, Harris RH, Awad WH. Flame retardant mechanism of a polymer clay nanocomposite. In Recent Adv. Flame Retard. Polym., Lewin (editor). vol. 14. Norwalk, USA: BCC, 2003. pp. 14-26
12. Ismail MR , Ali MAM, .El-Milligy AA, Afifi MS. Studies on sand/clay unsaturated polyester composite materials. *J. App. Poly. Sci*. 1999; **72**: 1031-1038
13. Suh DJ, Lim YT, Park OO. The property and formation mechanism of unsaturated polyester-layered silicate nanocomposite depending on the fabrication methods. *Polymer*, 2000; **41:** 8557-8563
14. Kornmann X, Berglund LA, Streteand J, Giannelis E P. Nanocomposites based on montmorillonite and unsaturated polyester. *Polymer Eng. Sci*. 1998; **38**:1351-1358
15. Fu X A, Qutubuddin S, Polymer-clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer* 2001; **41**: 807-813

16. Bharadwaj RK, Mehrabi AR, Hamilton C, Trujillo C, Murgs M, Fan R, Chavira A, Thompson AK. Structure-property relationships in cross-linked polyester-clay nanocomposites. *Polymer* 2002; **43**: 3699-3705
17. Kandola B, Nazaré S, Horrocks A. Thermal degradation behaviour of flame - retardant unsaturated polyester resins incorporating functionalised nanoclays. In *Fire Retardancy of Polymers: The use of mineral fillers in micro- and nano-composites*, Le Bras M, (eds). Royal Chemical Society: Cambridge, 2005; 147-160
18. Kandola B, Nazaré S, Horrocks A R. Effect of layered silicate nanocomposites on burning behaviour of conventionally flame retarded unsaturated polyesters, In *ACS Symp. Ser.*, 2005, in press.
19. Gilman JW, Bourbigot S, Bellayer S, Stretz H, Paul DR, in Fire Retardancy of Polymers New application of Mineral Fillers, Le Bras M. Wilkie CA, Bourbigot S, Duquesne S, Jama C (eds.), RC 2005, pp.177-186
20. Li B. A study of the thermal decomposition and smoke suppression of poly(vinyl chloride) treated with metal oxides using a cone calorimeter at a high incident heat flux. *Polym Deg Stab.* 2002; **78:** 349-356
21. Gilman JW, Jackson CL, Morgan AB, Harris Jr R, Manias E, Giannelis EP, Wuthenow M, Hilton D, Phillips SH. Flammability properties of polymer-layered silicate nanocomposites: Propylene and polystyrene nanocomposites. *Chem Mater* 2000; **12**: 1866-73.
22. Kashiwagi T, Harris RH Jr, Zhang X, Briber RM, Cipriano BH, Raghavan SR, Awad WH, Shields JR. Flame retardant mechanism of polyamide6- clay nanocomposites. *Polymer*. 2004; **45**: 881-891.

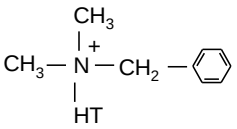
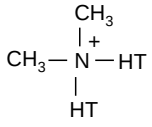
23. Qin H, Zhang S, Zhao C, Hu G, Yang M. Flame retardant mechanism of polymer/clay nanocomposites based on polypropylene. *Polymer.* 2005; **46**: 8386-8395.

24. Levchik SV. Halogen-free approach in fire retardancy of thermoplastic polyesters In *Recent Advances in Flame Retardancy of Polymers*, vol 13, Lewin M (ed). Business Communications Co Inc.: Norwalk, 2002; 296-314

25. Bourbigot S, Bras M LE, Dabrowaski F, Gilman JW, Kashiwagi T. PA-6 clay nanocomposites hybid as char forming agent in intumescent formulations. *Fire Mater*. 2000; **24**: 201-208

26. Beyer G. Flame retardant properties of EVA-nanocomposites and improvements by combination of nanofillers with aluminum trihydrate. *Fire Mater*, 2001; **25**:193-197

Table 1. Properties of organically modified clays

Clay code	Commercial name	Organic modifier	2θ (degrees)	d spacing (nm)
Na-MMT	Cloisite Na^+	-	7.3	1.17
Cl 10A	Cloisite 10A		4.5	1.92
Cl 15A	Cloisite 15A		2.8	3.15

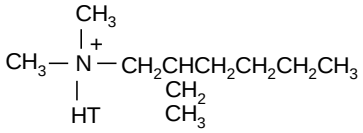
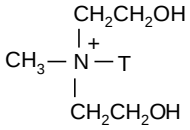
Cl 25A	Cloisite 25A		4.2	2.02
Cl 30B	Cloisite 30 B		5.1	1.76

Table 2. Mass percentages of various components in the formulations

Sample	Sample description	Resin (%)	Clay (%)	Flame retardant (%)
Res	Resin	100	-	-
Res/Cl	Resin+Clay	95	5	-
Res/FR	Resin + FR	83	-	17
Res/Cl/FR	Resin+Clay+FR	79	4	17

Table 3. Thermogravimetric and cone calorimetric data for processability studies for resin/clay and resin/clay/FR nanocomposite structures containing different levels of Cloisite 25A clay and constant APP loadings.

Sample description	Processability	TGA results* % Mass residue		Cone calorimetric data at 50 kW/m^2				
		600 ^{o}C (%)	800 ^{o}C (%)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	Hc (MJ/kg)	Smoke (l)
Res	√	1.1	1.0	34	1153	77.5	21.1	761
Res/MMA	√	-	-	32	1154	71.8	21.3	715
Res/MMA/Cl 5%	√	3.0	2.7	39	826	72.2	20.3	818
Res/MMA/Cl 7.5%	√	4.6	3.6	39	806	72.9	20.9	812
Res/MMA/Cl 10%	√	6.4	5.1	37	705	66.1	19.0	843
Res/APP 20%	√	23.1	4.0	31	456	50.1	16.0	754
Res/APP 30%	√	28.0	4.4	29	451	52.1	16.7	720
Res/ MMA/Cl 5%/APP 20%	√	**18.5**	**9.9**	**29**	**417**	**51.8**	**16.0**	**796**
Res/MMA/Cl 7.5%/APP 20%	×	19.5	11.1	-	-	-	-	-
Res/ MMA/Cl 10%/APP 20%	×	-	-	-	-	-	-	-
Res/MMA/Cl5%/APP 30%	×	28.8	9.2	-	-	-	-	-
Res/MMA/Cl 7.5%/APP 30%	×	27.1	12.8	-	-	-	-	-
Res/ MMA/Cl 10%/APP 30%	×	25.2	13.3	-	-	-	-	-

Key: TTI= Time to ignition, PHRR = Peak heat release rate and THR = Total heat released.

* Note: % silica content in the residue (from reference 17) has been accounted for.

Table 4. XRD data* for polyester-clay composites containing optimised levels of clay (5%) and FR (20%)

Sample	2θ (degrees)	d spacing (nm)	Change† in d spacing (nm)	Type of composite
Res/Cl 10A	5.0	1.79	-0.13	Microcomposite
Res/Cl 15A	**2.4**, 4.8	3.57, 1.85	+0.42	Intercalated nanocomposite
Res/Cl 25A	-	-	-	Exfoliated nanocomposite
Res/Cl 30B	4.7	1.86	+0.10	Intercalated nanocomposite
Res/APP	-	-	-	Microcomposite
Res/Cl10A/APP	5.0	1.74	-0.18	Microcomposite
Res/Cl15A/APP	**2.4**, 4.8	3.57, 1.85	+0.42	Intercalated nanocomposite
Res/Cl 25A/APP	-	-	-	Exfoliated nanocomposite
Res/Cl30B/APP	4.7	1.86	+0.10	Intercalated nanocomposite

*XRD data in the lower 2θ region (2-10^{o}) only.

† Change in d-spacing compared to respective clays from Table 1; +ve and – ve values indicate increase and decrease in d-spacings respectively.

Table 5. Cone calorimetric results for polyester-nanocomposite samples with optimized levels of clay (5%) and FR (20%) at 50 kW/m^2

Samples	Thickness (mm)	Mass	TTI (s)	FO (s)	PHRR (kW/m^2)	TTP (s)	FIGRA KW/s	THR (MJ/m^2)	Mass residue (%)	Hc (MJ/kg)	Total smoke (l)
Res	3.07	37.5	34	136	1153	100	11.5	77.5	2	21.1	761
Res/Cl 10A	**2.97**	**35.9**	**41**	**165**	**843**	**105**	**8.0**	**71.8**	**6**	**21.5**	**790**
Res/Cl 15A	3.00	35.9	36	160	872	100	8.7	74.1	6	21.9	823
Res/Cl 25A	3.05	35.8	36	147	887	100	8.9	69.3	5	20.4	763
Res/Cl 30B	3.03	36.4	37	158	844	100	8.4	71.2	6	20.8	781
Res/APP	**3.17**	**37.3**	**31**	**190**	**456**	**90**	**5.0**	**50.1**	**16**	**16.0**	**754**
Res/NH	3.00	37.6	33	205	451	105	4.5	61.8	11	18.5	684
Res/NW	2.27	34.2	30	159	722	95	7.6	57.4	8	18.2	1183
Res/ATH	3.30	39.7	38	198	597	130	4.6	64.5	13	18.7	683

Coefficient of variation for different parameters are: Thickness= 0-12%, Mass = 0-3%, TTI= 0-11%, FO = 1-10%, PHRR = 0-6%, THR = 0- 4%, H_c = 0.4-3.9%, Total smoke = 1-10%

Table 6. Combined effect of nanoclay (5%) and FR (20%) on cone calorimetric parameters of polyester resin at 50 kW/m^2

Samples	Thickness (mm)	Mass (g)	TTI (s)	FO (s)	PHRR (kW/m^2)	TTP (s)	FIGRA KW/s	THR (MJ/m^2)	Mass residue (%)	Hc (MJ/kg)	Total smoke (l)
Res/Cl 10A/APP	2.50	41.0	35	251	357	120	2.9	56.2	18	16.7	717
Res/Cl 15A/APP	2.50	39.7	32	217	476	85	5.2	52.6	18	16.2	674
Res/Cl 25A/APP	2.43	36.9	34	224	453	90	5.0	56.9	17	18.6	764
Res/Cl 30B/APP	2.33	37.7	34	217	415	70	5.9	54.4	17	17.4	724
Res/Cl 25A/NH	2.53	40.1	36	250	580	115	5.0	65.3	11	18.3	1145
Res/Cl 25A/NW	3.33	41.5	37	287	670	115	6.0	66.4	10	17.8	1274
Res/Cl 25A/ATH	3.07	40.1	44	223	515	135	3.8	57.9	17	17.4	690

Coefficient of variation for different parameters are: Thickness= 0-12%, Mass = 0-3%, TTI= 0-11%, FO = 1-10%, PHRR = 0-6%, THR = 0- 4%, H_c = 0.4-3.9%, Total smoke = 1-10%

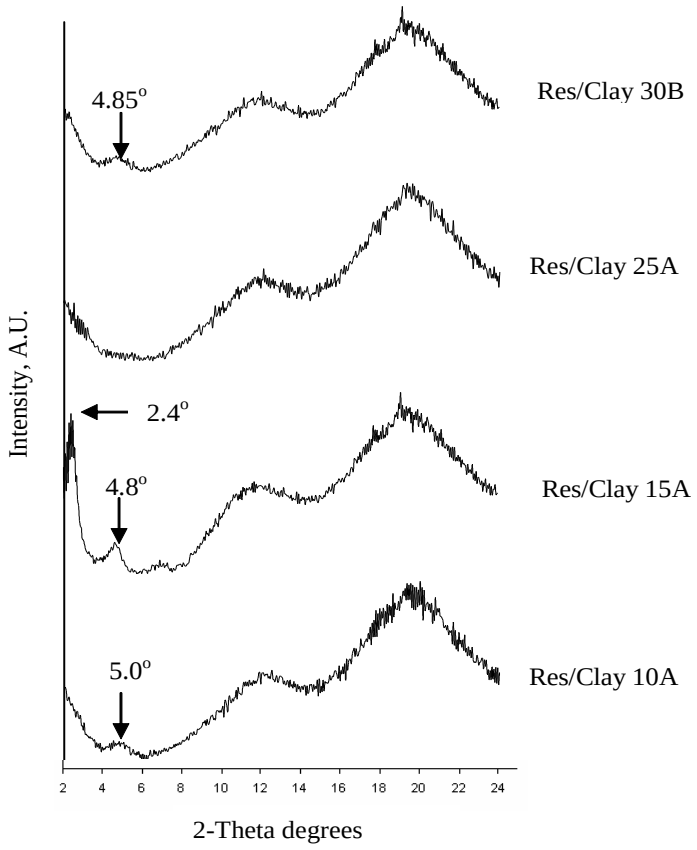


Figure 1(a) : XRD curves for various Res/Clay hybrids

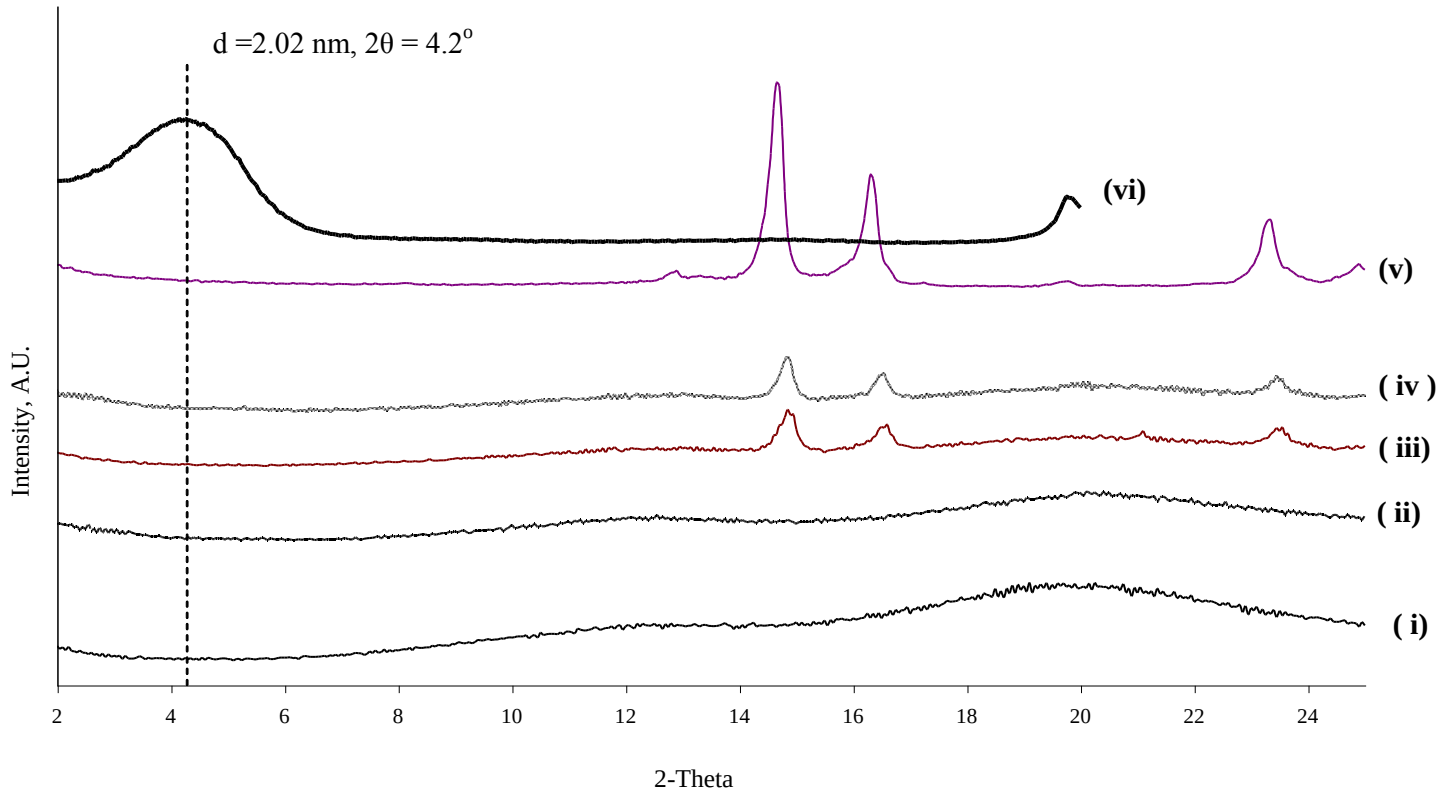


Figure1 (b). XRD graphs for (i) pure resin,(ii) Res/Cl 25A,(iii) Res/APP, (iv) Res/Cl 25A/APP,(v)APP and (vi) Cl 25A

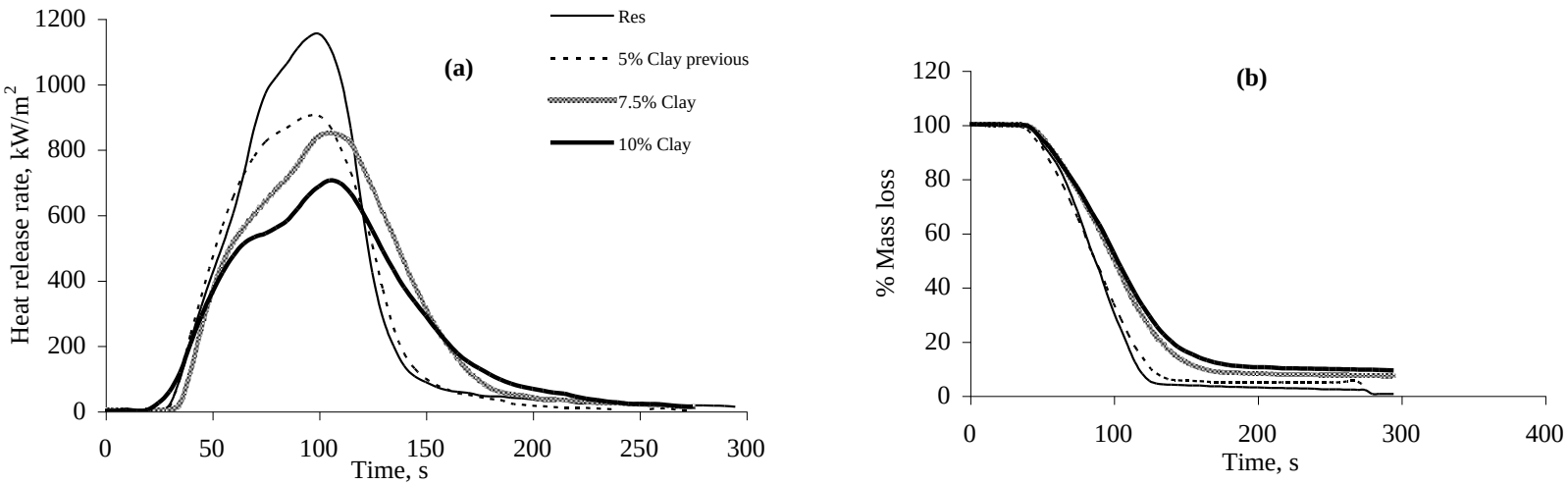


Figure 2 Cone calorimetric results for polyester resin and resin/clay nanocomposite structures containing different levels of Cloisite 25A clay loadings.

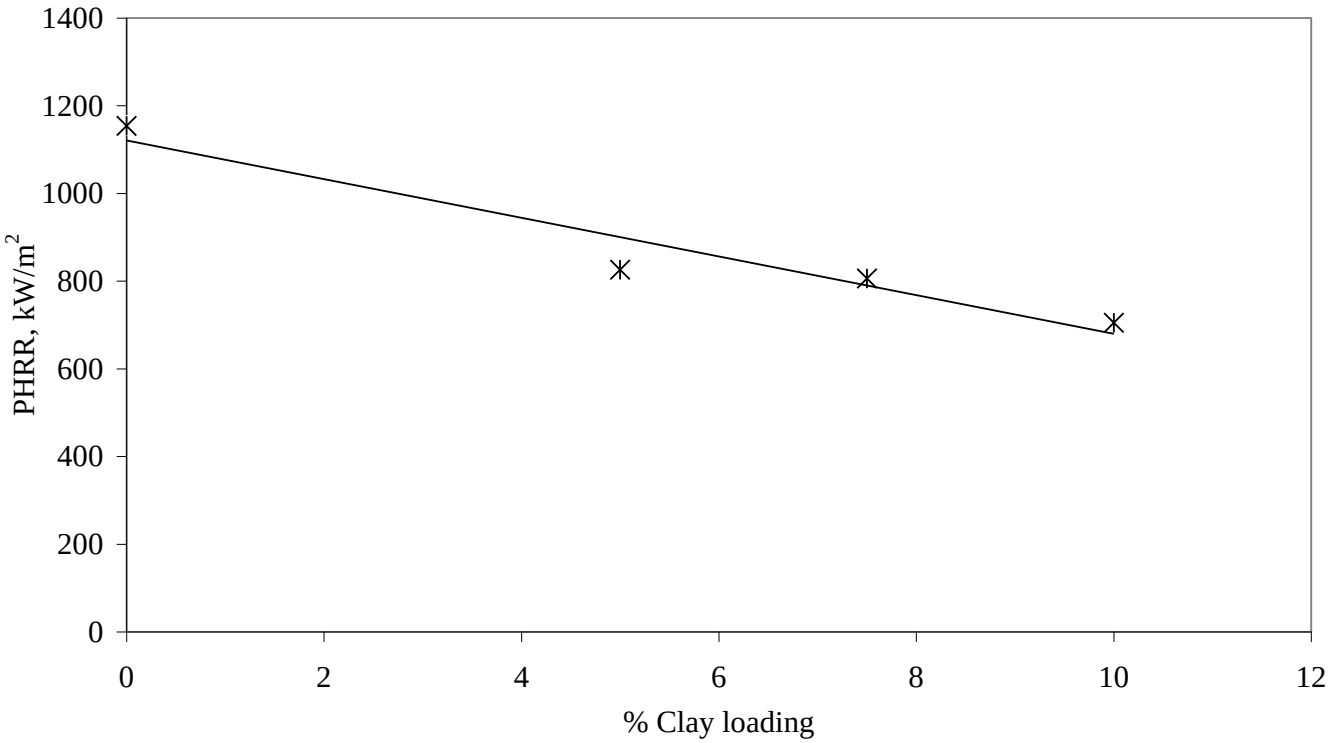


Figure 3. Effect of clay loading on PHRR values in Res/MMA/Cl formulations.

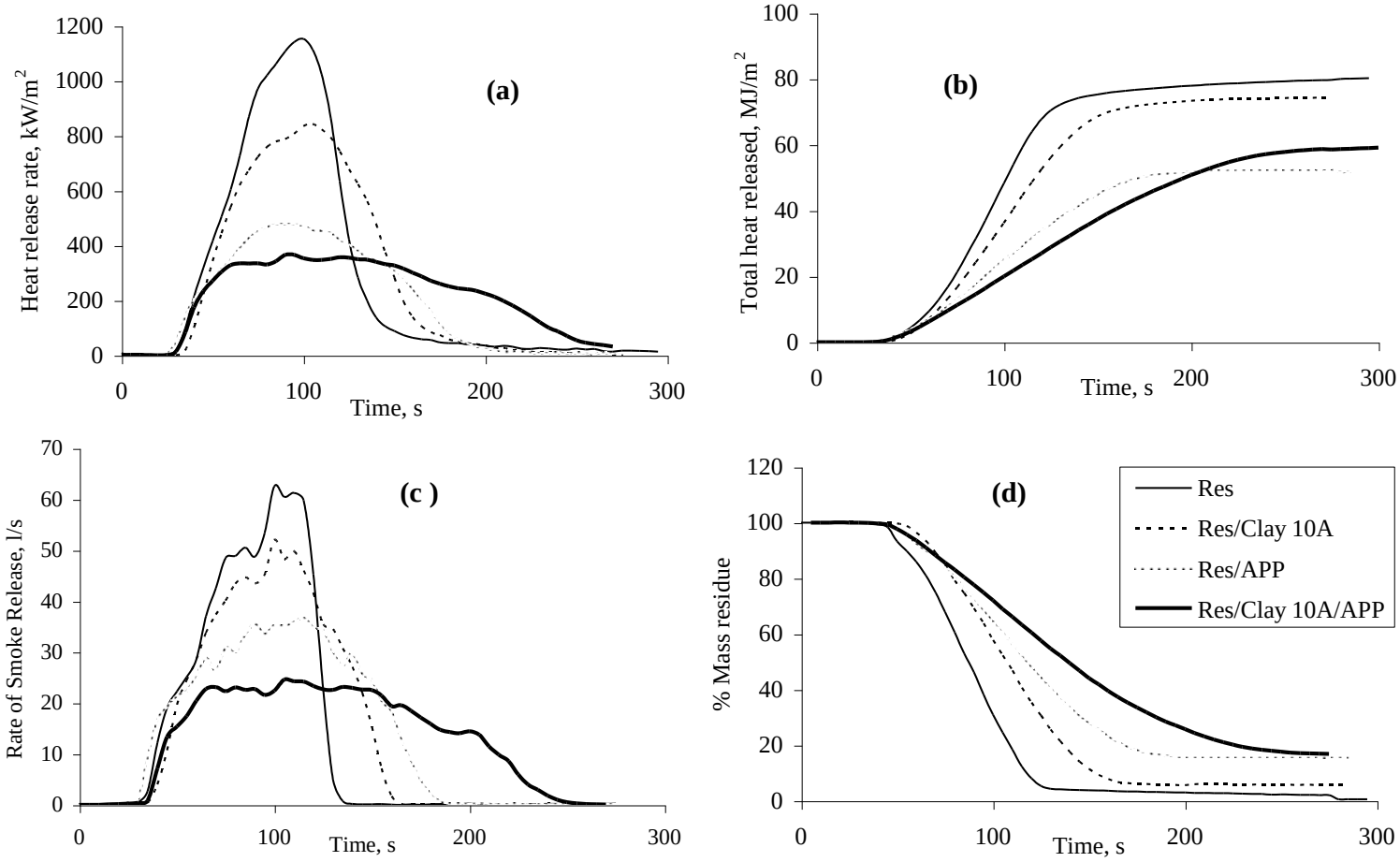


Figure 4. (a) HRR, (b) THR, (c) rate of smoke release and (d) mass loss versus time curves for pure polyester resin, Res/Clay (5%) hybrid, and flame retarded (20% APP) polyester resin with and without nanoclay Cl 10A.

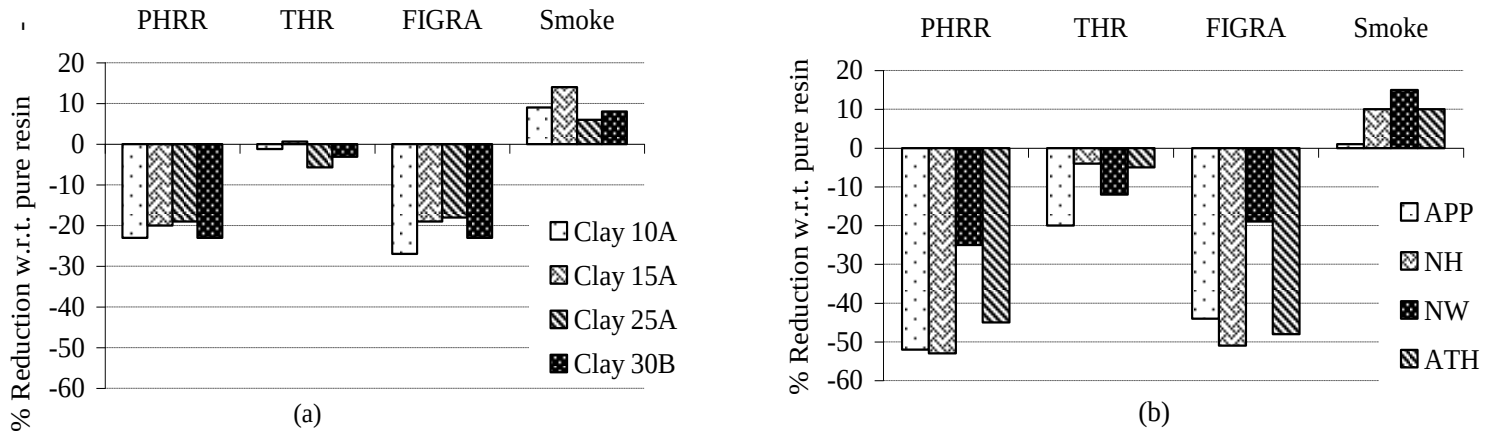


Figure 5. Burning behaviour with respect to pure resin of resin formulation containing (a) different functionalised clays at 5% (w/w) and (b) various flame retardants, at 20% (w/w).

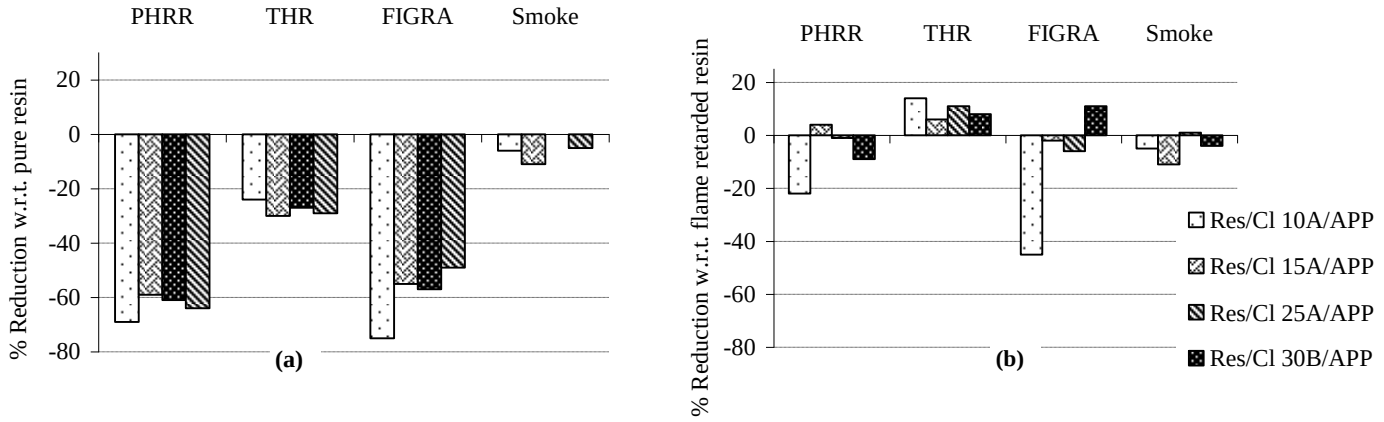


Figure 6. Burning behaviour of resin formulations containing different modified clays (5% w/w) and ammonium polyphosphate (20% w/w) with respect to (a) pure resin and (b) flame retarded resin formulation.

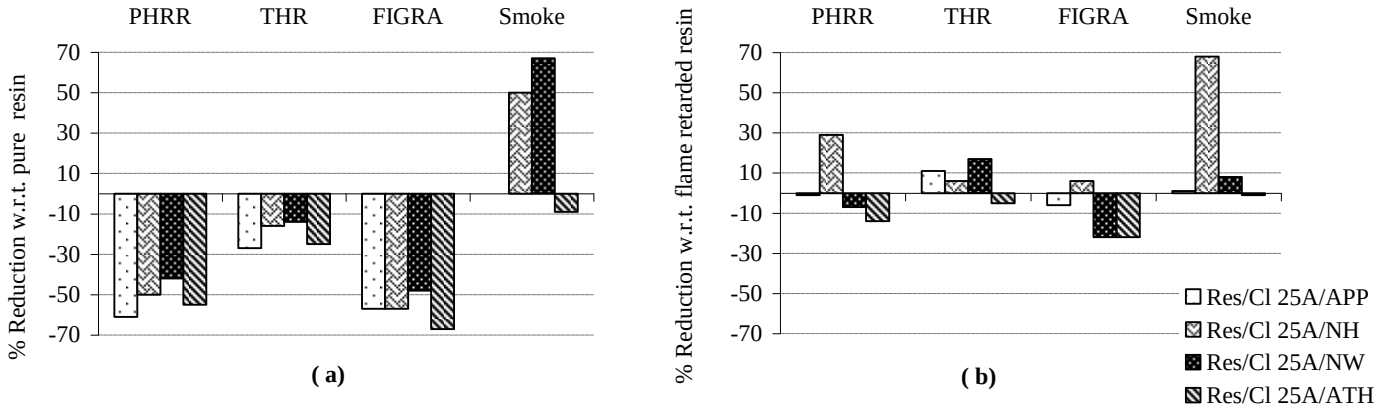


Figure 7. Burning behaviour of resin formulations containing Cl 25A (5% w/w) and different flame retardants (20% w/w) with respect to (a) pure resin and (b) respective flame retarded resin formulations.